

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

2,4,5 - Triphenylimidazole Dimers

We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of Wilmington 98, Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

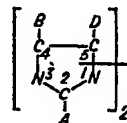
This invention relates to novel dimers of the 2,4,5 - triphenylimidazolyl radical.

Substances which change colour upon exposure to sunlight or a source of ultra-violet radiation but return to their original colour when the light source is removed are known as phototropic substances. An example of a phototropic compound is the oxidation product of lophine (2,4,5 - triphenylimidazole) which upon exposure to actinic radiation changes colour from a light lemon yellow to a reddish purple. This and other known phototropic materials have not been widely used, however, because they all possess one or more disadvantages, e.g. they are slow in reverting back to their original colour; the colour is fixed, i.e. no variation in colour can be obtained; only a comparatively low number of colour reversals is attained before compound failure; and they are adversely affected by heat (i.e. they are thermotropic).

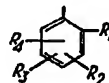
The present invention provides new phototropic substances which are 2,4,5 - triphenylimidazolyl dimers in which the phenyl group in the 2-position is substituted in at least one of the positions *ortho* to the imidazolyl ring with a group not containing an active hydrogen

atom. The term "active hydrogen atom" is used throughout this specification to denote a hydrogen atom capable of reacting with methyl magnesium iodide to give methane. The 2,4,5-triphenylimidazolyl dimer may have up to 4 substituents in the phenyl group in the 2-position and up to 3 substituents in each of the phenyl groups in the 4- and 5-positions.

The novel 2,4,5 - triphenylimidazolyl dimers of the invention are compounds of the formula:



wherein the valencies of the atoms in the imidazolyl rings, other than those through which the imidazolyl rings are joined, are satisfied by two conjugated intracyclic double bonds, and wherein A is a substituted phenyl radical of the formula:



wherein R₁ represents a substituent not containing an active hydrogen atom and R₂, R₃ and R₄ represent hydrogen or substituents free from active hydrogen atoms and where two of R₁, R₂, R₃ and R₄ in adjacent positions on the phenyl ring taken together may form a benzo

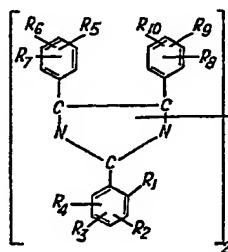
ring with the proviso that the substituent or substituents *ortho* to the imidazolyl radical have a sigma constant below 0.7; and B and D are phenyl groups which are unsubstituted or substituted with up to three substituents free from active hydrogen atoms, two of which, in adjacent positions on the phenyl ring, may together form a benzo ring; with the proviso that at least one of the *ortho* positions in each of the phenyl groups B and D is unsubstituted.

The groups B and D can be alike or different as will be shown more fully below. A discussion and explanation of the sigma value is given by H. H. Jaffe in Chem. Rev. 53, 191 (1953), particularly pages 219 to 223.

The substituents which are free from active hydrogen atoms include alkyl, alkoxy, alkoxy-carbonyl, alkylthio, dialkylamino, dialkylcarbamoyl, dialkylsulphamoyl, alkanoyloxy, N-alkylalkanamido, aryl, aryloxy, arylthio, benzo, halo, and cyano groups. The alkyl substituents and the alkyl groups of the alkoxy substituents can be of any chain length, but are preferably lower alkyls such as methyl, ethyl, propyl, butyl, isobutyl, sec. - butyl, tert. - butyl, pentyl, isopentyl. The alkanoyl and alkanamido substituents preferably contain from 1 to 6 carbon atoms, i.e. ranging from formyl to caproyl and ranging from formamido to caproamido, respectively. The aryl groups include phenyl, 1-naphthyl, 2-naphthyl and the halo substituents include bromine, chlorine and fluorine.

Groups which have a hydrogen atom capable of reacting with the Zerewitinoff reagent should be avoided because it has been found that these substituted biimidazoles either are non-phototropic or have a low order of phototropism and are readily converted upon light exposure to non-phototropic substances. Examples of the undesirable groups are hydroxyl, thiol, carboxyl, amino and alkylamino (-NHR). The amino and alkylamino groups are those of acylamido and sulphonamido as well as amino substituents attached directly to a phenyl ring.

Particularly preferred compounds of this invention are represented by the formula



wherein R_1 to R_{10} are alkyl groups, e.g. lower alkyl groups of 1 to 6 carbon atoms; alkoxy groups, e.g. alkoxy groups containing 1 to 6

carbon atoms; chlorine, bromine, or fluorine atoms; or substituents on adjacent carbon atoms in the phenyl ring together forming a benzo ring, e.g. an unsubstituted ring; with the proviso that at least one of the *ortho* positions in each of the phenyl groups B and D is unsubstituted.

The substituted triphenylimidazoles which are intermediates in the preparation of the new dimers can be prepared:

(A) by refluxing, in glacial acetic acid containing ammonium acetate, benzil with an appropriately substituted benzaldehyde or a benzil and benzaldehyde which are both suitably substituted. The reaction product is precipitated by drowning the reaction mass, e.g. in water or an ammonium hydroxide solution, and is recovered by filtration. The product can then be purified by recrystallization from a solvent. This procedure is described by Davidson *et al.* in J. Org. Chem. 2, 319 (1937);

(B) by refluxing a benzoin and a benzaldehyde in methanol in the presence of copper acetate and ammonia. This is an adaptation of the procedure of Wiedenhagen *et al.*, Ber 70, 570 (1937); or

(C) by heating a benzil and a benzaldehyde at 180° to 190°C . in formamide solution as disclosed in Belgian Patent Specification No. 589,417.

The dimers of the invention can be prepared by oxidising the corresponding 2,4,5-triphenylimidazole in a liquid reaction medium. Potassium ferricyanide in aqueous alkaline solution is the preferred oxidising agent. For example the substituted triphenylimidazole in ethanol containing potassium hydroxide can be oxidized to a dimer of the imidazole compound by treatment with aqueous potassium ferricyanide. The desired product precipitates from the reaction mixture, is isolated by filtration and is washed free from ferricyanide with water. This procedure is described, for compounds not within the scope of the present invention, by Hayashi *et al.* in Bull. Chem. Soc. Japan, 33, 565 (1960). The substituted triphenylimidazole may also be oxidized in solution with lead dioxide, eg. by agitating a benzene or chloroform solution of the imidazole with lead dioxide (PbO_2) or by passing a saturated solution of the imidazole in benzene through a column packed with PbO_2 and diatomaceous earth. The products can be recrystallized from benzene or cyclohexane. Difficulty may be encountered in the dimerization if the triphenylimidazole contains more than two substituents having sigma constants of 7.0 and above. The dimers obtained, however, are phototropic compounds.

The dimer exists in a number of conceivable isomeric structures which are differentiated by the manner in which the radicals are linked together. The isomers of the phototropic

- dimer which have been isolated differ in spectral properties and thermotropic properties. A more stable dimer can be isolated from standard preparative procedures such as are described above. A less stable dimer has been formed by irradiation of a solvent solution, e.g. toluene, containing a biimidazole compound at a temperature at or below -30°C. The less stable isomer of the dimer has been found to give on heating a more intensely coloured solution at lower temperatures than the more stable dimer.
- The biimidazole compounds are identified by elemental analysis and molecular weight determination. They are characterized by melting point, colour, the colour developed by phototropism, colour life, i.e. time to revert to natural state after shutting off the source of radiation; infrared, visible, and ultraviolet absorption spectra, and by thermotropism and piezotropism (response to change in pressure) when such properties exist for a particular compound.
- Substituted dimers of 2,4,5 - triphenylimidazolyl radicals, as defined in this invention, are set forth in the following table wherein the substituents are present on the phenyl groups as designated in the table:

Substituents of phenyl rings attached to imidazolyl radical at

2-Position	4-Position	5-Position
<i>o</i> -acetoxy	—	—
<i>o</i> -benzyl	—	—
2,3-benzo (1-naphthyl)	—	—
2,3-benzo	2,3-benzo	—
2,3-benzo	2,3-benzo	2,3-benzo
2,3-benzo	<i>p</i> -methoxy	<i>p</i> -methoxy
3,4-benzo-2-methoxy (2-(1-methoxy)naphthyl)	—	—
4,5-benzo-2-methoxy (2-(3-methoxy)naphthyl)	—	—
<i>o</i> -benzylthio	<i>o</i> -benzylthio	<i>o</i> -benzylthio
<i>o</i> -bromo	—	—
<i>o</i> -bromo	<i>p</i> -bromo	—
<i>o</i> -bromo	<i>o</i> -methoxy	<i>o</i> -methoxy
2-bromo-4-phenyl	—	—
<i>o</i> -butoxy	—	—
<i>o</i> -t-butoxy	—	—
<i>o</i> -t-butyl	—	—
<i>o</i> -t-butyl	<i>p</i> -t-butyl	<i>p</i> -t-butyl
<i>o</i> -N-butylacetamido	—	—
<i>o</i> -butylthio	—	—
<i>o</i> -butyryloxy	—	—
<i>o</i> -chloro	—	—
<i>o</i> -chloro	<i>o</i> -chloro	—
<i>o</i> -chlor	<i>p</i> -chloro	—

Substituents of phenyl rings attached to imidazolyl radical at

2-Position	4-Position	5-Position
<i>o</i> -chloro	<i>o</i> -chloro	<i>o</i> -chloro
<i>o</i> -chloro	3,4-dichloro	—
<i>o</i> -chloro	<i>m</i> -pentyloxy	—
<i>o</i> -chloro	<i>m</i> -pentyloxy	<i>m</i> -pentyloxy
<i>o</i> -chloro	<i>p</i> -propionyloxy	—
2-chloro-4-phenyl	—	—
<i>o</i> -cyano	—	—
<i>o</i> -cyano	<i>p</i> - <i>t</i> -butyl	—
<i>o</i> -cyano	<i>p</i> - <i>t</i> -butyl	<i>p</i> - <i>t</i> -butyl
<i>o</i> -cyano	<i>p</i> -cyano	<i>p</i> -cyano
<i>o</i> -cyano	<i>p</i> -methoxy	<i>p</i> -methoxy
2,3,4,5-dibenzo (9-phenanthryl)	—	—
2,3-dibromo	—	—
2,4-dibromo	—	—
2,6-dibutyl	—	—
2,4-di- <i>t</i> -butyl	—	—
2,4-di- <i>t</i> -butyl	2,4-difluoro	—
2,4-di- <i>t</i> -butyl	<i>p</i> -fluoro	<i>p</i> -fluoro
<i>o</i> -dibutylsulphamoyl	—	—
2,4-dichloro	—	—
2,4-dichloro	<i>o</i> -bromo	—
2,4-dicyano	<i>p</i> -cyano	<i>p</i> -cyano
2,6-dicyano	—	—
2,4-diethoxy	—	—
<i>o</i> -diethylsulphamoyl	—	—
2,5-difluoro	<i>p</i> -cyano	—

Substituents of phenyl rings attached to imidazolyl radical at

2-Position	4-Position	5-Position
2,5-difluoro	<i>p</i> -cyano	<i>p</i> -cyano
2,3-dimethoxy	—	—
2,4-dimethoxy	—	—
2,4-dimethoxy	<i>o</i> -chloro	—
2,4-dimethoxy	<i>o</i> -chloro	<i>o</i> -chloro
2,4-dimethoxy	2,4-dimethoxy	—
2,4-dimethoxy	2,4-dimethoxy	2,4-dimethoxy
2,4-dimethoxy	<i>o</i> -methoxy	—
2,4-dimethoxy	<i>p</i> -methoxy	—
2,4-dimethoxy	<i>m</i> -phenylthio	—
2,4-dimethoxy	<i>m</i> -phenylthio	<i>m</i> -phenylthio
<i>o</i> -dimethylamino	—	—
<i>o</i> -dimethylamino	<i>p</i> -dipentylamino	—
<i>o</i> -dimethylamino	<i>o</i> -dipropylsulphamoyl	—
<i>o</i> -dimethylcarbamoyl	—	—
2,4-dinaphthylthio	—	—
2,4-dipentyl	2,4-dipentyl	2,4-dipentyl
2,4-dipentyl	3,4-benzo (2-naphthyl)	3,4-benzo
<i>o</i> -dipentylamino	—	—
2,4-dipropoxy	—	—
2,4-dipropoxy	<i>o</i> -diethylcarbamoyl	—
<i>o</i> -dipropylcarbamoyl	—	—
<i>o</i> -ethoxy	—	—
<i>o</i> -ethoxycarbonyl	—	—
<i>o</i> -ethyl	—	—
<i>o</i> -N-ethylbutyramido	—	—
<i>o</i> -N-ethylpropylamino	—	—
<i>o</i> -ethylthio	—	—

Substituents of phenyl rings attached to imidazolyl radical at

2-Position	4-Position	5-Position
<i>o</i> -N-ethylvaleramido	<i>p</i> - <i>t</i> -pentyl	<i>p</i> - <i>t</i> -pentyl
<i>o</i> -fluoro	—	—
<i>o</i> -fluoro	<i>o</i> -methoxy	<i>o</i> -methoxy
<i>o</i> -methoxy	—	—
<i>o</i> -methoxy	<i>p</i> -chloro	—
<i>o</i> -methoxy	<i>p</i> -methoxy	—
<i>o</i> -methoxy	<i>o</i> -methoxy	<i>o</i> -methoxy
<i>o</i> -methoxy	<i>p</i> -methoxy	<i>p</i> -methoxy
<i>o</i> -methoxy	<i>o</i> -methylthio	<i>o</i> -methylthio
<i>o</i> -methoxy	<i>p</i> -nitro	—
<i>o</i> -methoxy	<i>p</i> -nitro	<i>p</i> -nitro
<i>o</i> -methoxy	<i>p</i> -phenylsulphonyl	—
<i>o</i> -methoxy	<i>p</i> -phenylsulphonyl	<i>p</i> -phenylsulphonyl
<i>o</i> -methoxycarbonyl	—	—
<i>o</i> -methoxycarbonyl	3,4-benzo	—
<i>o</i> -methoxycarbonyl	<i>p</i> -N-ethylphenyl- phamoyl	—
2-methoxy-4-phenyl	—	—
<i>o</i> -methyl	—	—
<i>o</i> -methyl	<i>p</i> -benzoyloxy	<i>p</i> -benzoyloxy
<i>o</i> -N-methylacetamido	<i>o</i> -N-ethylbutyramido	<i>o</i> -N-ethylbutyramido
<i>o</i> -N-methylacetamido	<i>o</i> -N-methylacetamido	—
<i>o</i> -N-methylacetamido	<i>o</i> -N-methylacetamido	<i>o</i> -N-methylacetamido
<i>o</i> -N-methylpropionamido	—	—
<i>o</i> -methylthio	—	—
<i>o</i> -1-naphthyl	<i>p</i> -phenoxy	—

Substituents of phenyl rings attached to imidazoyl radical at

2-Position	4-Position	5-Position
<i>o</i> -2-naphthyl	—	—
<i>o</i> - <i>t</i> -pentyl	—	—
<i>o</i> -pentyloxy	—	—
<i>o</i> -pentyloxycarbonyl	—	—
<i>o</i> -pentyloxycarbonyl	3,4-benzo	3,4-benzo
<i>o</i> -9-phenanthryl	<i>p</i> -methoxy	<i>p</i> -methoxy
<i>o</i> -phenoxy	—	—
<i>o</i> -phenoxy	3,4,5-trimethoxy	3,4,5-trimethoxy
<i>o</i> -phenyl (2-biphenyl)	—	—
<i>o</i> -phenyl	<i>p</i> -methoxycarbonyl	<i>p</i> -methoxycarbonyl
<i>o</i> -phenyl	<i>m</i> -pentyloxycarbonyl	—
<i>o</i> -phenyl	<i>m</i> -pentyloxycarbonyl	<i>m</i> -pentyloxycarbonyl
<i>o</i> -phenyl	<i>p</i> -phenyl	<i>p</i> -phenyl
<i>o</i> -phenylthio	<i>p</i> -1-naphthylthio	<i>p</i> -1-naphthylthio
<i>o</i> -propoxy	—	—
2,4,6-tribromo	—	—
2,4,6-tributyl	—	—
2,4,6-tri- <i>t</i> -butyl	—	—
2,3,5-trichloro	—	—
2,4,6-trichloro	—	—
2,4,6-trichloro	<i>o</i> -butylthio	—
2,4,6-tricyano	<i>p</i> -cyano	<i>p</i> -cyano
2,4,6-triethoxy	—	—
2,4,6-trimethoxy	—	—
2,4,6-tri- <i>t</i> -pentyl	—	—
2,4,6-tripropoxy	—	—

The invention is illustrated by the following Examples. The quantities stated in the Examples are parts by weight unless otherwise designated.

5

EXAMPLE I

To 2.1 parts of benzil (0.01 mole) dissolved in 50 parts of glacial acetic acid containing 6 parts of ammonium acetate (0.078 mole) was added 1.4 parts of *o*-chlorobenzaldehyde (0.01 mole), and the solution was refluxed for

20

Calculated: %C=76.3, %H=4.6, %N=8.5
Found: %C=76.7, %H=4.7, %N=8.2

To 1.1 parts of the above prepared imidazole dissolved in 100 parts of ethanol containing 12 parts of potassium hydroxide was added 450 parts of a 1% by weight water solution of potassium ferricyanide at a rate of 5 parts per minute for 1.5 hours with continuous stirring. The oxidation reaction product in an amount of 1.0 part precipitated from the reaction mixture, was isolated by filtration, and was washed with water until free from ferricyanide. The product was dried at 56°C. for eight hours at 0.1 mm mercury pressure

45

Calculated: %C=75.4, %H=4.7, %N=8.1
Found: %C=75.9, %H=4.7, %N=8.1

A portion of the ethanol-solvated product was dried azeotropically with cyclohexane to produce non-solvated material.

50

A colourless 0.5% benzene solution of this biimidazole turned purple immediately on exposure to sunlight and the colour faded within a minute after shutting out the light. A control solution of the dimer of 2,4,5-triphenylimidazolyl radical required 15 minutes to fade after the light exposure. In another measurement for colour life, the benzene solution was irradiated in a quartz cell 1 cm. thick for 1 minute supported 3-½ inches from a 275-watt sun lamp (General Electric RS) and placed in a spectrophotometer for a recording of the change with time in the optical density (D) of the maximum absorption band at 545 mu. A reading was also obtained after the solution had been kept in the dark overnight and used as an "infinity" reading (D_{∞}). A plot of $1/(D -$

65

$D_{\infty})$ vs. time (minutes) gave a line whose slope

90

Calculated: %C=69.0, %H=3.9, %N=7.7
Found: %C=69.0, %H=4.0, %N=7.4

1.2 Parts of the imidazole was oxidized to the dimer of 2-(2,4-dichlorophenyl)-4,5-

2 hours. The solution was then drowned in 200 parts of cold water whereupon 3.1 parts of reaction product precipitated. The product was isolated by filtration and purified by recrystallizing twice from ethanol. The product, 2-(*o*-chlorophenyl)-4,5-diphenylimidazole, is a white crystalline solid having a melting point of 196°—197°C. and the following analysis:

15

after predrying overnight in a vacuum oven at 50°C. It was solvated with two moles of ethanol for every three moles of biimidazole. The product, a dimer of 2-(*o*-chlorophenyl)-4,5-diphenylimidazolyl radical is a pale yellow crystalline solid which softens at about 90°C. and melts to form a yellow gel at 95 to 110°C. The compound turns lavender at 170°C., becomes red-brown at 190°C. and at 220°C. it becomes red. Analysis for the solvated biimidazole:

35

40

represented the colour fading rate of the phototrope and provided a reproducible quantitative value of this property for comparison with a control compound not having an ortho-substituent in the 2-phenyl ring and other phototropes. The value obtained for the 2-(*o*-chlorophenyl)-4,5-diphenylimidazolyl radical, i.e. the slope of the above graph was 7.3 compared with 0.46 for the unsubstituted triphenylimidazolyl radical, that is, the radical from the new compound fades about 16 times as fast as the radical from the unsubstituted compound.

70

75

80

EXAMPLE II

By the procedure of Example I, 1.75 parts of 2,4-dichlorobenzaldehyde (0.01 mole) was reacted with the benzil to produce 3.5 parts of 2-(2,4-dichlorophenyl)-4,5-diphenylimidazole, a white, crystalline solid having a melting point of 174.5—175°C. and the following analysis:

85

95

ample I. The product was obtained in 81% yield as a pale yellow phototropic solid. It softens at 90°C., forms a gel at 115°C., becomes a yellow liquid at 133°C., turns red at 210°C., becomes orange at 250°C., and decomposes at 262°C. Analysis for the unsolvated biimidazole was:

Calculated: %C=69.2, %H=3.6, %N=7.7
Found: %C=69.3, %H=4.2, %N=7.4

10 A 0.5% benzene solution of the above product turned purple on exposure to sunlight, the colour fading in 45 seconds. From optical density measurements of the 558m μ adsorption band obtained as described in Example I, the colour fading rate value was 17, indicating a fading rate of about 35 times that of the 2,4,5-triphenylimidazolyl radical with a value of 0.46 taken as a control. 20

15 The solid material turns purple on exposure to light and reverts to the original pale yellow colour when taken from the light. 20
EXAMPLE III
o - Anisaldehyde in an amount of 1.4 parts was reacted with 2.1 parts of benzil as described in Example I to produce 2.9 parts (90% yield) of 2 - o - anisyl - 4,5 - diphenylimidazole. This imidazole is a white, crystalline solid having a melting point at 207.5—208.5°C. and the following analysis: 25

30
Calculated: %C=81.0, %H=5.6, %N=8.6
Found: %C=80.8, %H=5.6, %N=8.5

35 When 1.1 parts of the imidazole was oxidized with potassium ferricyanide according to the procedure of Example I, 0.96 part of a pale green phototropic 2 - (o - anisyl) - 4,5 - diphenylimidazolyl dimer was produced. On heating, this material softens at 160°C., remaining pale green. On continued heating it darkens to brown and turns red when the temperature reaches 210°C. On exposure to light at room temperature the biimidazole turns a weak blue. Identity of the product was confirmed by the following analysis for a material solvated on the average with 2 moles of ethanol for every 3 moles of biimidazole: 40 45

Calculated: %C=80.0, %H=5.6, %N=8.2
Found: %C=79.8, %H=5.4, %N=8.6

50 A 0.5% benzene solution turned weak blue when irradiated with sunlight. The colour fading rate value by optical density measurement of the maximum absorption band at 612 m μ obtained as described in Example I was 7.7 vs. 0.46 for the unsubstituted triphenylimidazolyl radical, indicative of a fadeout in less than a minute. 60

65
Calculated: %C=77.5, %H=5.7, %N=7.9
Found: %C=77.9, %H=5.8, %N=8.0

70 Upon oxidation with potassium ferricyanide the imidazole was converted in 91% yield to the dimer of the 2 - (2,4 - dimethoxyphenyl) - 4,5 - diphenylimidazolyl radical, a pale green phototropic solid. Analysis of a portion of the product which was isolated in an unsolvated state was:

Calculated: %C=77.7, %H=5.4, %N=7.9
Found: %C=77.2, %H=5.8, %N=7.8

75 The solid turned blue-green when exposed to light and reverted to a pale green when removed from the light. A benzene solution also turned blue-green on light exposure and exhibited a colour fading rating value of 0.82 by measurement of the change of the optical density of the 611 m μ absorption band in the spectrophotometer within a time range as described in Example I. Such a value indicates a colour fading rate essentially two times that 80

of the unsubstituted triphenylimidazolyl radical.

EXAMPLE V

1 - Naphthaldehyde (1.6 parts) was condensed with benzil in the presence of am-

monium acetate as described in Example I to produce in 99% yield 2 - (1 - naphthyl) - 4,5 - diphenylimidazole as a white crystalline solid having a melting point of 289.5—290°C. and an analysis:

Calculated: %C=86.7, %H=5.2, %N=8.1
Found: %C=87.0, %H=5.2, %N=8.2

By treatment with potassium ferricyanide the imidazole was oxidized to the dimer of 2 - (1 - naphthyl) - 4,5 - diphenylimidazolyl

radical, a pale green solid phototrope having in the unsolvated state the following analysis:

Calculated: %C=86.9, %H=5.0, %N=8.1
Found: %C=86.6, %H=5.2, %N=8.1

With heating this biimidazole exhibits at 85°C. a brightening of the green colour. At 130°C. the colour fades to a yellow. The compound softens at 153°C. and forms a yellow gel at 165°C. On cooling the material to room temperature and reheating these changes may be repeated.

The solid material turns orange on exposure to sunlight and reverts to a pale yellow-orange when withdrawn from the light. A dilute colourless benzene solution turns green when radiated and gives a colour fading rating value of 1.2 when the change in the optical density

of the 467 mμ band is measured as described in Example I. Such a value indicates a colour fading rate which is over 2.5 times that of the unsubstituted triphenylimidazolyl radical with a value of 0.46.

EXAMPLE VI

When 1.9 parts of *o* - bromobenzaldehyde was used in place of the *o*-chlorobenzaldehyde in Example I, 3.6 parts (97% yield) of 2-(*o*-bromophenyl) - 4,5 - diphenylimidazole was produced. This product is a white crystalline solid melting at 205.5°—206.5°C. and having the following analysis:

Calculated: %C=67.2, %H=4.0, %N=7.5
Found: %C=67.8, %H=4.4, %N=7.4

1.3 Parts of the imidazole was oxidized with potassium ferricyanide as described in Example I, the compound being converted to a dimer of 2 - (*o* - bromophenyl) - 4,5 - diphenylimidazolyl radical, in 90% yield. This dimer is a pale yellow solid which softens at

106°C. and forms a yellow gel at 120°C. Its identity was confirmed by the following analysis of the material isolated as a product solvated on the average with 2 moles of ethanol for every 3 moles of biimidazole:

Calculated: %C=66.8, %H=4.1, %N=7.2
Found: %C=66.8, %H=4.0, %N=7.2

Irradiation of the solid biimidazole under a sun lamp gave a purple coloration. A purple solution formed at once when an essentially colourless 0.5% benzene solution of the phototrope was similarly irradiated, and the colour faded in about a minute when the light was turned off. A measurement, as described in Example I, of the rate of colour fading by recording the change in the optical density of the 550 mμ absorption band following the

irradiation gave a value of 7.4, which is about 16 times the fading rate of the unsubstituted triphenylimidazolyl radical.

EXAMPLE VII

2 - (*o* - Fluorophenyl) - 4,5 - diphenylimidazole was made in 99% yield by reacting 1.2 parts of *o* - fluorobenzaldehyde with benzil as described in Example I. The product is a white crystalline solid melting at 205.5—206°C. It gave the following analysis:

Calculated: %C=80.2, %H=4.8, %N=8.9
Found: %C=80.0, %H=4.9, %N=8.9

- When 1.0 part of the imidazole was reacted with potassium ferricyanide in an ethanol solution of potassium hydroxide as was done in Example I, the dimer of a 2-(*o*-fluorophenyl)-4,5 - diphenylimidazolyl radical was produced in a 78% yield. This biimidazole is a pale yellow solid which softens at 139°—149°C., formed a gel at 158°C., and changes to a yellow-brown liquid at 165°C.
- The photographic biimidazole containing one mole of water per mole of compound analyzed as follows:

Calculated: %C=78.3, %H=4.7, %N=8.7
Found: %C=78.6, %H=4.8, %N=8.6

- Upon irradiation by direct or indirect (through window glass) sunlight or by a sun lamp the pale yellow compound in the solid state turns purple, and the colour fades when the radiation is stopped. An essentially colourless benzene solution, of 0.5% concentration, is also coloured purple when it is exposed to this radiation and soon reverts to the colourless condition when the solution is removed from the light or the light is shut off. A quantitative measurement, as described in Example I, of the rate of colour fading by recording the change in optical density of the maximum absorption band for the colored solution at 548 m μ gives a rate value of 6.2 or shows the imidazolyl radical having a fluorine substituent in an ortho position of the 2 - phenyl group to have a colour life about 1/13 that of the unsubstituted compound, the latter having a fading rating of 0.46.

EXAMPLE VIII

- A solution of dimethyl formamide containing 10% by weight of cellulose acetate (essentially completely acetylated) and 0.1% by weight of the dimer of 2 - (*o* - chlorophenyl) - 4,5 - diphenylimidazolyl radical prepared as described in Example I was spread on a glass plate and was dried by the application of mild heat from an infrared heat lamp utilizing sufficient ventilation. The glass plate was placed in a window frame and when illuminated in the sunlight a pleasing pink colour quickly developed. The glass plate reverted to its essentially colourless state in a matter of seconds when the source of illumination was not present.
- By using the procedure described in Example I above with the appropriate substituted benzaldehyde or 9 - phenanthrene carboxaldehyde, the following substituted biimidazoles were prepared:
- a dimer of 2 - (*o* - ethoxyphenyl) - 4,5 - diphenylimidazolyl radical.
- This compound is a light yellow solid which softens at 138°C., and becomes a green gel at 140° to 145°C. and a clear green liquid at 154°C. A further effect is observed when the green liquid turns brown between 165 and 180°C. and orange at 218°C. On light exposure at room temperature a benzene solution of the compound turns blue, and the colour decays in about 5 minutes in the dark. The identity of the compound was confirmed by the following analysis of unsolvated material.

- Calculated: %C=81.4, %H=5.64, %N=8.25
Found: %C=80.8, %H=5.65, %N=8.15;

a dimer of the 2 - (2,3 - dimethoxyphenyl) - 4,5 - diphenylimidazolyl radical.

- This is a light yellow solid which softens at 95°C. and becomes a yellow gel at 104°C., a yellow liquid at 140°C., orange at 160°C., red-orange at 180°C., and brown in colour at 200°C. An irradiated benzene solution of the compound turns purple and loses its colour in the dark in about 6 minutes. A chemical analysis was as follows:

- Calculated for the material solvated on the average with one mole of ethanol for every two moles of compound: %C=77.0, %H=5.63, %N=7.64
Found: %C=76.95, %H=5.70, %N=7.68;

a dimer of the 2 - (9 - phenanthryl) - 4,5 - diphenylimidazolyl radical.

- This biimidazole is a pale pink solid which turns yellow and softens at 165°C. and becomes a yellow gel at 180°C. and a yellow liquid at 230°C. In a benzene solution the compound turns yellow orange when irradiated and loses the colour in the dark in less

than two minutes. An analysis of the material solvated on the average with one mole of ethanol for every two moles of compound:

Calculated: %C=87.2, %H=4.91, %N=7.00
Found: %C=87.2, %H=4.6, %N=7.00.

- 5 Additional dimer compounds prepared by the procedure of Example I include the dimer of 2 - (2,4,6 - trimethylphenyl) - 4,5 - diphenylimidazolyl radical giving a violet colour, having a colour life of about 7 minutes and a fading rate of 1.0;

a dimer of 2 - (*o* - methoxyphenyl) - 4 - (*p* - methoxyphenyl) - 5 - phenylimidazolyl radical giving a blue colour, having a colour life of about 4 minutes and a fading rate of 1.61;

a dimer of 2 - (α - naphthyl) - 4,5 - di - (*p* - methoxyphenyl)imidazolyl radical giving a green colour, having a colour life of about 7 minutes and a fading rate of 1.01 as measured at 660 m μ ; and

a dimer of 2 - (*o* - methoxyphenyl) - 4,5 - di - (*p* - methoxyphenyl)imidazolyl radical, which gives a blue colour and has a fading rate of 0.50.

- 25 All the above dimers have fading rates faster than their isomeric compounds which do not contain a substituent in the ortho position of the phenyl ring in the 2-position.

- 30 The novel dimers of the substituted imidazolyl radical are useful as the colour-reversing components of light-activated sun shades or shields. Addition of these dimers to plastic interlayers for laminated glass, or to coatings deposited on transparent substrates, such as glass, plasters, and the like are extensions of this concept. These photosensitive composition and coatings are useful in spectacle lenses where they protect the wearer from sudden high-intensity solar or industrial radiation. The materials when utilized on a car windshield improve the safety factor because the windshield of a car in passing from a light to a dark area, e.g. a tunnel, loses its colour and reverts to its original clear, colourless condition. The materials are also useful for the same purpose with transparent materials which act as a substitute for glass.

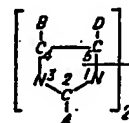
- 45 An advantage of this invention is that the above described dimers of the imidazolyl radical having at least one of the enumerated substituents in an ortho position in the 2-phenyl ring surprisingly and unexpectedly have a markedly improved fading rate (i.e. rapid colour decay or short colour life) over a corresponding dimer but one containing no ortho substituent in the 2 - phenyl ring. In addition, the ortho-substituted dimer is less thermotropic i.e. requires a higher temperature to effect a colour change than the corresponding dimer.

- 60 Another advantage of this invention is that by varying the substituents in positions other than *ortho* in the 2-phenyl ring, a variety of

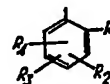
colour shades, or an alteration in the colour shade upon exposure to light is obtained. It is also possible to alter other properties by changing the substituents in positions other than *ortho* in the 2-phenyl ring, e.g. to change the melting point, to improve the solubility in a selected solvent, etc.

WHAT WE CLAIM IS:—

1. A 2,4,5-triphenylimidazolyl dimer having the general formula:



wherein the valencies of the atoms in the imidazolyl rings, other than those through which the imidazolyl rings are joined, are satisfied by two conjugated intracyclic double bonds, and wherein A is a substituted phenyl radical of the formula:



wherein R₁ represents a substituent not containing an active hydrogen atom and R₂, R₃, and R₄ represent hydrogen or substituents free from active hydrogen atoms and where two of R₁, R₂, R₃, and R₄ in adjacent positions on the phenyl ring taken together may form a benzo ring; with the proviso that the substituent or substituents *ortho* to the imidazolyl radical have a sigma constant below 0.7; and B and D are phenyl groups which are unsubstituted or substituted with up to three substituents free from active hydrogen atoms, two of which, in adjacent positions on the phenyl ring, may together form a benzo ring; with the proviso that at least one of the *ortho* positions in each of the phenyl groups B and D is unsubstituted.

2. A 2,4,5 - triphenylimidazolyl dimer according to claim 1, wherein the substituents on the phenyl radicals in the groups A, B and D are alkyl groups containing up to six carbon atoms, alkoxy groups containing up to six carbon atoms, chlorine, bromine or fluorine atoms, or substituents on adjacent carbon atoms together forming a benzo ring.

3. The dimer of the 2 (*o* - chlorophenyl) - 4,5 - diphenylimidazolyl radical.

4. The dimer of the 2 - (2,4 - dimethoxyphenyl) - 4,5 - diphenylimidazolyl radical.

5. The dimer of the 2 - (2,4 - dichlorophenyl) - 4,5 - diphenylimidazolyl radical.
6. The dimer of the 2 - (1 - naphthyl) - 4,5 - diphenylimidazolyl radical.
- 5 7. The dimer of the 2 - (*o* - methoxyphenyl) - 4,5 - diphenylimidazolyl radical.
8. The dimer of the 2 - (*o* - bromophenyl) - 4,5 - diphenylimidazolyl radical.
9. The dimer of the 2 - (*o* - fluoroprenyl) - 4,5 - diphenylimidazolyl radical.
- 10 10. The dimer of the 2 - (*o* - ethoxyphenyl) - 4,5 - diphenylimidazolyl radical.
11. The dimer of the 2 - (2,3 - dimethoxyphenyl) - 4,5 - diphenylimidazolyl radical.
- 15 12. The dimer of the 2 - (9 - phenanthryl) - 4,5 - diphenylimidazolyl radical.
13. The dimer of the 2 - (2,4,6 - trimethylphenyl) - 4,5 - diphenyl imidazolyl radical.
- 20 14. The dimer of the 2 - (*o* - methoxyphenyl) - 4 - (*p* - methoxyphenyl) - 5 - phenylimidazolyl radical.
15. The dimer of the 2 - (1 - naphthyl) - 4,5 - di(*p* - methoxyphenyl)imidazolyl radical.
16. A 2,4,5 - triphenylimidazolyl dimer according to claim 1, substantially as described. 25
17. Process for the production of a 2,4,5 - triphenylimidazolyl dimer as claimed in any one of the preceding claims, which comprises oxidizing the corresponding 2,4,5 - triphenylimidazolyl in a liquid reaction medium. 30
18. Process according to claim 17, wherein the 2,4,5 - triphenylimidazole is oxidized with potassium ferricyanide in aqueous alkaline solution. 30
19. Process according to claim 17, wherein the 2,4,5 - triphenylimidazole in solution is oxidized with lead dioxide. 35
20. Process for the production of a 2,4,5 - triphenylimidazolyl dimer according to claim 17, substantially as described. 40

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